(11) (A) No. 981444

(45) ISSUED Jan. 13, 1976

(52) CLASS 33-49
C.R. CL.

(19) (CA)

CANADIAN PATENT

(54) POLARIZATION INTERFEROMETER WITH BEAM POLARIZING AND RETARDING MEANS

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(21) APPLICATION No. 227,395
(22) FILED May 21, 1975 Div'n of Appl'n No. 171,282 filed May 14, 1973

(30) PRIORITY DATE May 15, 1972 (253,303) U.S.A.

No. OF CLAIMS 7

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CCA-274 (2-74)

ABSTRACT OF THE DISCLOSURE

Interferometer means of improved design is provided in dichroism measurement apparatus that includes:

a) a source of linearly polarized electromagnetic radiation of different wavelengths λ,

b) the improved interferometer means for processing source radiation to provide a beam characterized, for each wavelength, by ellipticity that alternates between left and right circular polarization and between which the beam polarization becomes linear in one direction as the ellipticity alternates from left to right circular polarization, and linear in another direction as the ellipticity alternates from right to left circular polarization, the characteristic frequency ν_a of such alternation varying as a function of the wavelength,

c) a sample space located for effecting passage of the elliptically polarized beam through a dichroic sample in that space, the sample differentially absorbing the alternately polarized radiation of a characteristic set of wavelengths λ, and

d) a beam intensity detector located in the path of the beam passing from the sample space and characterized as having signal output that varies in intensity with frequency ν_a when said sample is in said space, said output adapted for processing to produce dichroic spectra varying with wavelength λ.

The interferometer means comprises a beam splitter located for passing and reflecting source light in two beams, beam reflecting and polarizing structures in the respective paths of said two beams, at least said reflecting structures being relatively movable, and actuating means for effecting such relative movement of said structures to control said frequencies ν_a.

BACKGROUND OF THE INVENTION

This invention relates generally to apparatus for measuring polarization-dependent optical properties of samples, and more particularly concerns the application of interferometric techniques with associated scanning in such measurements.

In the past, and as exemplified in U. S. Patent 3,257,894, the measurement of circular dichroism (a very useful optical property of substances, and defined as the difference in absorption of an optically active sample when determined using left-circularly polarized light and then right-circularly polarized light), has involved the step of obtaining the ratio of alternating and direct current components of an electrical signal obtained at the output of a detector such as a phototube. Light incident upon the detector, and resulting in production of that signal, is typically derived by transmission as a beam from a source including a monochromator and through a polarizer, then through a polarization or electro-optic modulator wherein the linear polarized light is elliptically polarized in a cyclically varying manner (characterized by two counter-rotating, circularly polarized components, the relative magnitudes of the two components changing cyclically in time -- at a "modulation frequency" -- so that the dominant component is alternately right- and left-circularly polarized), and finally through a sample. The latter, when circularly-dichroic, absorbs unequally the circularly polarized components of opposite sense and of periodically varying polarization, so that the total amount of light incident upon the phototube undergoes a corresponding periodic variation, i.e. larger when the predominant circularly polarized component of the light passing through the sample is of the sense absorbed to lesser degree by the sample, and smaller when the predominant circularly polarized component is of the sense absorbed to greater degree by the sample. The fluctuating component of the phototube output is of frequency equal to the

modulation frequency and with amplitude proportional to the difference between transmission levels for the circularly polarized components of opposite sense. The DC component on the other hand corresponds to the average or mean transmission of the sample for light at the wavelength of interest.

The above and similar systems require the provision of much expensive equipment, including the monochromator and electro-optic modulator. While much thought has been given to the possible elimination of such equipment, the principles of operation as outlined above remain embodied in existing apparatus for measuring dichroism in samples, i.e. successful substitutes have not been found.

Equipment for measuring circular dichroism is usually easily adapted to the measurement also of linear dichroism, defined as the difference in absorption of a sample for linearly polarized light with the direction of polarization corresponding to maximum absorption by the sample and a direction orthogonal to the maximum absorption direction. Linear dichroism is another useful optical property of substances and is the property upon which, for instance, the useful characteristics of sheet polarizers such as *"Polaroid" depend. It may be measured by the equipment described above by introducing a 1/4 wave "bias" in the polarization characteristics of the light beam by superimposing a sufficient unidirectional potential upon the electro-optical modulator in addition to the alternating potential, or by inserting in the light beam a 1/4 wave retarder of conventional design. The light beam passing through the sample then varies cyclically between two orthogonal linearly polarized components. At the modulation frequency a linearly dichroic sample absorbs these two components unequally producing corresponding periodic variations in the amount of light incident upon the phototube.

Existing systems, as will be evident from the above description,

*Trademark

also are limited in that measurements of dichroism spectra must be made one wavelength band at a time, the bands being changed in succession by a scanning mechanism in the monochromator. This is particularly troublesome in the infrared region of the spectrum where, owing to the very small amounts of dichroism ordinarily encountered, and to the below mentioned "constant noise" property of usual photometric detection systems, a very long time must be taken for the measurement at each wavelength band in order to accumulate enough information to permit accurate estimates of such small differences in absorption.

In ordinary absorption measurements, it has been known for some time that by using methods commonly called "Fourier spectroscopy," employing an interferometer, measurements could be made at many wavelengths simultaneously, each wavelength being characterized by a different signal frequency imposed on the radiation falling on the detector. The signals are subsequently "sorted out" according to frequency by a mathematical process characterized by taking the inverse Fourier transform of the signals collected and electrically recorded from the detector. By making measurements at many wavelengths simultaneously, it is possible to obtain as accurate or more accurate measurements at each wavelength as could have been obtained in the same time at a single wave band with the use of a monochromator for wave band isolation, assuming constant detector noise, equal optical bandwidth or resolution, equal transmission efficiency, and equal "light grasp" or "throughput."

Another advantage of interferometric modulation lies in the fact that it is practical for a given resolving power of the apparatus to transmit more radiation through an interferometer than through a monochromator. This is for two reasons: The first is that the "light grasp," that is, the geometrical factor determining the capability of the apparatus to transmit radiation, is recognized to be greater for an interferometer than for a

monochromator. The second is that the monochromator usually contains many more optical elements, each of which introduces some loss in the system; thus, the transmission efficiency of the monochromator can easily be less even for a given single wavelength than that for an interferometer despite the fact that a typical beam splitter in an interferometer reduces the light intensity transmitted through the interferometer by a factor of two at the beam recombining point, half of the radiation being returned toward the source.

Prior to the invention disclosed in U.S. Letters Patent 3,728,030, issued April 17, 1973, and entitled, "Polarization Interferometer," no way was known, to my knowledge, to apply the above interferometric modulation technique to the measurement of circular dichroism. The Hawes application discloses an interference polarization modulator, including relatively movable reflectors for processing source light, and characterized by production of negligible amplitude modulation in the absence of dichroism in the optical train that follows the modulator and in the detector. Either linear or circular dichroism in that region of the instrument, however, will convert the polarization modulation into amplitude modulation. The polarization modulation is characterized by a different frequency for each wavelength of the radiation: thus, the signals caused by the interaction of the radiation with dichroic sample may all be recorded simultaneously and may subsequently be "unscrambled" by simple electronic frequency isolation, or, preferably, by the use of a computer to derive the inverse Fourier transform of the ensemble of frequencies constituting the complete signal, and thus obtaining a transmission spectrum corresponding to the dichroism. The transmission spectrum in turn, in the case of the circular dichroism, may be converted into dichroism by dividing by the ordinary transmission spectrum (corresponding to ordinary absorption) which may be derived by

ordinary Fourier spectroscopy.

While the specific polarization interferometer means described in said Hawes patent has certain unusual advantages, there are additional unusual advantages associated with the interferometer means described herein.

SUMMARY OF THE INVENTION

It is a major object of the invention to provide interferometer means of improved design in dichroism measurement apparatus of the above type. Generally speaking, that apparatus will include:

a) a source of linearly polarized electromagnetic radiation of different wavelengths λ.

b) the improved interferometer means for processing source radiation to provide a beam characterized, for each wavelength, by ellipticity that alternates between left and right circular polarization and between which the beam polarization becomes linear in one direction as the ellipticity alternates from left to right circular polarization, and linear in another direction as the ellipticity alternates from right to left circular polarization, the characterisitc frequency ν_a of such alternation varying as a function of the wavelength,

c) a sample space located for effecting passage of the elliptically polarized beam through a dichroic sample in that space, the sample differentially absorbing the alternately polarized radiation of a characteristic set of wavelengths λ, and

d) a beam intensity detector located in the path of the beam passing from the sample space and characterized as having signal output that varies in intensity with frequency ν_a when said sample is in said space, said output adapted for processing

to produce dichroic spectra varying with wavelength λ.

As will be seen, the improved interferometer means may comprise a beam splitter located for passing and reflecting source light in two beams, beam reflecting and polarizing structures in the respective paths of said two beams, at least said reflecting structures being relatively movable, and actuating means for effecting such relative movement of said structures to control said frequencies ν_a. More specifically, the polarizing structures may each comprise a reflection polarizer; or, a mirror together with a transmission polarizer located to pass the beam both incident upon and reflected from the mirror; or, a set of retroreflectors located to separate the beam entering the set from the beam leaving the set, together with a transmission polarizer in the path of that beam, as will be seen.

Alternatively, the improved interferometer means may comprise a beam splitter as referred to , beam reflecting structures in the respective paths of the two beams, said structures being relatively movable, beam retarding means in the path of at least one of the two beams, and actuating means for effecting such relative movement of said structures as to control the frequencies ν_a. The said structures may comprise mirrors or retroreflectors; and the beam retarding means may comprise a quarter wave retarder in the path of the beam transmitted twice by the retarder, or a half wave retarder in the path of the beam transmitted once by the retarder; also, another half wave retarder may be employed and operated as a compensator in the path of the beam transmitted by the beam splitter.

More particularly, there is provided in dichroism measurement apparatus the combination that incldues a source of electromagnetic radiation of a relatively broad band of

wavelengths λ, and a linear polarizer in the path of the radiation. An interferometer for processing linearly polarized source radiation to provide a beam characterized, for each wavelength, by ellipticity that alternates between left and right circular polarization and between which the beam polarization becomes linear in one direction as the ellipticity alternates from left to right circular polarization, and linear in another direction as the ellipticity alternates from right to left circular polarization, the characteristic frequency ν_a of such alternation varying as a function of the wavelength. A sample space is located for effecting passage of the elliptically polarized beam through a dichroic sample in that space, the sample differentially absorbing the alternately polarized radiation of a characteristic set from the wavelengths λ. A beam intensity detector located in the path of the beam passing from the sample space and characterized as having signal output that varies in intensity with frequency ν_a substantially only when the sample is in the space, the output adapted for processing to produce dichroic spectra varying with wavelength λ. The means comprising a beam splitter located for passing and reflecting source light in two beams and beam reflecting structures in the respective paths of the two beams. The structures are relatively movable. A beam retarder in the path of at least one of the two beams and an actuator for effecting such relative movement of the structures to control the frequencies ν_a. The two beams return toward the splitter as separate but coherent beams and with relative and progressive phase retardation for recombination by the splitter and having orthogonal polarization directions to provide the elliptically polarized beam.

These and other objects and advantages of the invention, as well as the details of illustrative embodiments, will be

more fully understood from the following description and drawings, in which:

DRAWING DESCRIPTION

Fig. 1 is an overall system diagram;

Figs. 1a--1d are views taken normal to the beam locations as seen in Fig. 1;

Fig. 2 is a diagram illustrating fluctuation of polarization as a function of time, for two wavelengths;

Fig. 3 is a waveform illustrating dichroism as a function of wavelength;

Fig. 4 is a polarization sequence as is characteristic of the invention;

Fig. 5 is a polarization sequence as is characteristic of a conventional electro-optical modulator; and

Figs. 6-9 are partial system diagrams showing other modified forms of the invention.

DETAILED DESCRIPTION

Referring first to Fig. 1, having to do with measurement of circular dichroism, a light source and collimating lens are indicated at 10 and 11, the source providing broadband electromagnetic radiation such as light of different wavelengths λ. An aperture stop appears at 110. Between the source and the sample space 12 is located what may be referred to generally as polarization interferometer means including beam reflecting and polarizing structures for processing source light to provide a beam at 13 characterized, for each wavelength, by ellipticity that alternates between left and right circular polarization and between which the beam polarization becomes linear with direction alternating from one which may be referred to as "parallel" or "p", to one which may be referred to as "perpendicular" or "s", such notation being conventional, the frequency ν of such alternation being a function of light wavelength, i.e.

$$\nu_a = F(\lambda_a) \qquad (1)$$

where a = numbers associated with particular wavelengths

ν_a = ellipticity alternation frequencies associated with particular wavelengths

Fig. 2 depicts such fluctuation of polarization as a function of time t, for particular wavelengths λ_1, and λ_2, and may be generalized to other wavelengths by including lines of other slopes representative of other wavelengths, each passing through the zero optical phase axis at the zero order point. Note that the lines extend indefinitely in both directions, and that their extent depends upon the velocity and distance travelled by the movable carriage to be described. In the interferometer of Fig. 1, the slope of each line is inversely proportional to the corresponding wavelength.

The sample space 12 is located for effecting passage of the beam 13 through, for example, a circularly dichroic sample 14 in that space, the sample typically differentially absorbing the left and right circularly polarized light of a characteristic wavelength. A beam intensity detector 15 is located in the path of the beam 13<u>a</u> that has passed from the sample space 12, a condenser or other optics 16 typically being inserted in the beam path to reduce the size of the beam at the detector. A lens or other optics 16<u>a</u> may focus the beam 13 at the sample in space 12. An alternative sample space is indicated at 12<u>a</u>, other locations also being useful. The intensity of the detector output signal at 17 is characterized as varying with frequencies ν_a when the sample 14 is in the space 12.

The detector output, an interferogram function $F(\nu_a)$, is subsequently processed by apparatus generally designated at 18 to produce dichroic spectra varying with wavelength λ, as seen in Fig. 3.

In the absence of a sample, the detector ideally produces a

constant (or DC) output, except for noise or random fluctuations. The term "ideally" is used because a detector which is completely free of response to linear polarization is very unusual. In practice, advantage is taken of the fact that the circular dichroism is at quadrature with the signal resulting from linear effects, and can, therefore, in principle, be completely isolated from the linear response in the computation. In practice, of course, this isolation is never complete, but by careful adjustment and design it may be very helpful.

The illustrated apparatus 18 may include an amplifier 19 the input of which is connected to receive the detector output 17; a digitizer 20 (as for example an analog to digital converter) connected to receive the analog output 21 of the amplifier to provide a corresponding digital output 22; and a digital computer 23 operatively connected with the digitizer to derive a Fourier transmittance dichroism spectrum $\Delta T_{L-R}(\lambda)$ or $\Delta T_{p-s}(\lambda)$ as indicated, and in accordance with the equation $\Delta T_{(L-R)}$ or $\Delta T_{(p-s)} = \int F(\nu_a) \times M(\lambda_a)\, d\nu$, the demodulation function $M(\lambda)$ being defined below. A usable computational technique is described at page 1667 of the article "What is the Fast Fourier Transform?", proceedings of the IEEE, Vol. 55, No. 10.

A Fourier spectroscopy transmittance spectrum $T(\lambda)$ is derived for the ordinary transmission of the same sample, as is conventional, and the computer component 23a then divides $\Delta T_{L-R}(\lambda)$ or $\Delta T_{p-s}(\lambda)$ by $T(\lambda)$ to obtain at output point 90 the negative of the approximate absorbance spectrum $\Delta A_{L-R}(\lambda)$ or $\Delta A_{p-s}(\lambda)$ corresponding to circular or linear dichroism respectively, as is represented in Fig. 3. A linear or circular dichroism display is indicated at 91 in Fig. 1. If desired, output 21a from the digitizer may be recorded by recorder 24 for later processing by the computer. An alternative method for deriving the spectrum $T(\lambda)$ would merely involve turning the initial polarizer 26 so that its polarization effect

lies at 45° to the direction shown, followed by re-running the system and computation of the integral defined above. Alternatively, the spectrum $T(\lambda)$ may be obtained by merely removing the polarizer, which would be preferable if measuring linear dichroism. The interferometer means to provide beam 13 may have an associated scan velocity V characterized in that, for any selected wavelength λ_a of the light provided by source 10, there is an associated frequency ν_a of beam ellipticity alternation as described above, and as may for example be represented by the following equation:

$$\nu_a = \left(\frac{2V}{\lambda a} \right) \qquad (2)$$

This equation represents one form which Equation (1) may take, and means to be described will, in general, function to satisfy Equation (2). Equation (2) may be looked upon as representing the condition that each wavelength λ_a goes through the polarization cycle at a characteristic speed. Thus, in Fig. 2, wavelength λ_1, goes through the polarization cycle with a period T_1 associated with frequency ν_1; whereas, the wavelength λ_2 goes through its polarization cycle with a period T_2 associated with frequency ν_2, T_2 being different from T_1, in general. Note that these occur for the same scan velocity V of relatively movable reflecting structures in the interferometer means to be described.

In Fig. 1, the linear polarizer 26 operates upon source light 27 to linearly polarize same, as for example is represented by the vector 28 as viewed in Fig. 1a. A beam splitter 30 is located for reflecting a component of light beam 29 to form reflected beam 31, and for passing a component of beam 29 to produce beam 32.

A reflection polarizer, designated at 38, is movable relative to the reflection polarizer 35, and to the splitter 30, and also on the positive or negative Y-directions, and at velocity V, as described. For this purpose, the reflection polarizer 38 may be mounted on a carriage 36

movable by actuator 37. The reflection polarizer (one example of which is Model 186-0240 sold by Polaroid Corporation used as a reflector) produces a beam 48 returning to the splitter 30 with a characteristic polarization vector oriented in the X direction indicated by vector 49 as seen in Fig. 1b. Beam 48 is shown for convenience as offset from beam 31; however, normally these beams are coincident.

Reflection polarizer 35 operates upon beam 32 to produce a return beam 42 with polarization in the direction of vector 43 in the direction of the Z-axis, as seen in Fig. 1c. In this regard, polarizer 35 may be of the same type as polarizer 38. Beams 42 and 48 are recombined at the splitter 30 to produce beam 13, with associated polarization modulation described below in connection with Fig. 4. In this regard, the time coordinate t as

shown in Fig. 2 may be looked upon as determining the phase difference $\Delta\varnothing$ between vector 43 and vector 49, or as corresponding to the distance of travel of actuator 37. Beams 42 and 48 are separate but coherent linearly polarized beams of approximately equal intensity, and having orthogonal polarization directions; also, one of these beams is progressively retarded in phase with respect to the other, the retardation rate being different for different wavelengths within the band.

The fundamental requirement here is not of particular directions, but that the recombined polarization directions be orthogonal. More accurately, the separate beams which are recombined by the interferometer, if considered independently of each other, must be coaxial and have polarization vectors lying in orthogonal directions. While Fig. 1d shows these directions as X and Z, it is not at all necessary that one of these directions be the Z-direction and the other the Y- or X-direction; however, it is important that the two beams of linearly polarized radiation, which are recombined by the interferometer and which have polarization vectors as described above, do not have a resulting component that fluctuates substantially in intensity or amplitude. Otherwise the instrument would respond to ordinary absorption, and this much larger effect would tend to mask any circular dichroism as well as altering the apparent magnitude of any linear dichroism. The described interferometer can be adjusted to produce substantially no amplitude modulation of the combined beams at 13.

It should be noted that a carriage 36a for reflection polarizer 35 may be moved in the X-direction with velocity V, while carriage 36 is not moved in the Y-direction, the fundamental requirement being relative movement between the reflection polarizers.

A demodulation function M (λ) referred to above may be derived by operation of means for determining the position of the traveling carriage 36 with respect to the position where the two beam paths are equal as regards travel between the splitter and the reflector groups 35 and 38 and return (i.e. the so-called "zero-order" position). Such means may include a pair of auxiliary light beams, say in the visible region of the spectrum. One beam is a broad band beam 80 emanating from a source 81 to be polarized by a polarizer 98, and passing through the interferometer in offset relation to the beams 29, 31, 48, 32, 42 and 13 referred to above, but with the same total optical pathlengths between beam splitting and recombination. After recombination, the resultant beam at 82 is passed through a polarizer 75 or other strongly linearly dichroic device, and detected at 83 and the resultant signal is passed at 84 to the computer component 23b. The interferogram produced by this beam has a single strong spike or intensity maximum occuring approximately at the zero-order position, and thus identifying it and determining the zero phase position of the demodulation function M (λ).

The second beam 85 is a laser beam, generated at 86, and preferably having only one or a few axial modes, and being strongly linearly polarized. After passage through the interferometer in offset relation to the above discussed beams, but with the same optical pathlengths, the recombined resultant beam 87 is passed through a polarizer shown as 76, although the same dichroic element 75 may be used if desired, and detected at 88 and passed at 89 to the computer component 23b embodying a fringe counting and measuring system which enables the determination of the distance traveled by the carriage to be absolutely and accurately fixed, as by counting fringes from the zero-order position. The output of the fringe counting

system is then interpreted by the computer component 23b to provide the demodulation cosin or sine function M (λ), i.e. cos ($\omega_a t$) or sin ($\omega_a t$), required for the generation of the inverse

Fourier transform, the cosine or sine corresponding respectively to linear or to circular dichroism, whichever is to be measured.

Samples exist which exhibit both linear and circular dichroism simultaneously. For a complete study the interferogram of such a sample would have to be processed in the computer twice, once with each demodulation function, and the two separate (linear and circular) dichroism spectra of such a sample would then be obtained. The circular dichroism spectrum would show absorption bands which always correspond to some of the wavelength positions for ordinary absorption, whereas the linear dichroism spectrum would not necessarily correspond to the ordinary absorption spectrum although it would commonly do so. To reiterate, the one interferogram carries the information for both linear and circular dichroism spectra.

Reference to Fig. 4 shows the modulation character of the recombined beams at 13 as passing through the repeated cyclic sequence of which the following is a complete cycle with arbitrary starting point:

101 - left circularly polarized
102 - elliptically polarized (left)
103 - linearly polarized in the "p" direction
104 - elliptically polarized (right)
105 - right circularly polarized
106 - elliptically polarized (right)
107 - linearly polarized in the "s" direction
108 - elliptically polarized (left)
101 - left circularly polarized
etc.

This sequence illustrates only discrete points in a continuous progression of elliptical polarization that results if two coherent beams of polarized radiation are combined coaxially and with their polarization

vectors orthogonally oriented, and the phase of one beam is progressively increased with respect to the other.

As is conventional in absorption Fourier spectroscopy, the mirror motion may be either stepwise or continuous. Likewise, either the absolute value of the intensity or its differential with respect to pathlength may be measured. The apparatus shown in Fig. 1 may be looked upon as one example of means to produce the above polarization sequence.

An important difference between the Fig. 4 polarization sequence and that produced by conventional electro-optical modulators (as for example that described in U. S. Patent 3,257,894 to Grosjean) is that in the Fig. 4 sequence the linear phases at 103 and 107 are different, whereas in the sequence produced by the electro-optical modulator the linear phases have the same vector direction. See for example the linear phases 103 in the Fig. 5 sequence as produced by a conventional electro-optical modulator. The latter sequence progresses cyclically through five of the states shown in Fig. 4, beginning with the first state 101 or the third state 103 depending upon whether circular or linear dichroism is to be measured. It then returns through the same sequence in reverse, instead of progressing through the states 106, 107 and 108 as in Fig. 4. The Fourier modulator progresses through the complete cycle and then, continuing on, repeats the cycle again in the original sequence.

It is important that a clear distinction be made between operation in the infrared and operation in the ultraviolet or visible regions of the spectrum. It is well known that in the infrared, where measurements are not limited by the statistical arrival of photons, but rather by noise arising in the detector or in the amplifier used with the detector, or caused by the radiation field to which the detector is exposed on all sides, so that the noise per unit frequency bandwidth is substantially independent of the light intensity, the advantage in signal-to-noise ratio attainable

through Fourier spectroscopy is much larger than when measurements are made with a good multiplier phototube. In the latter, the noise principally arises from the statistical distribution of arrival of photons and thus increases with the total light intensity falling on the detector. Thus, with the phototube, each added wavelength band included increases the noise in proportion to the square root of the total flux of photons. The increasing noise vitiates the gain which would otherwise occur in signal-to-noise ratio. In other words, while Fourier dichroism measurements may have advantages in the ultraviolet or visible regions of the spectrum, these advantages do not include the so-called "Fellgett advantage," namely that the time for measurement of a large number of bands simultaneously by Fourier Spectroscopy is approximately equal to that required for measurement of a single band by conventional spectroscopy using a monochromator to isolate the wavelength band wanted and to reject other bands.

The modified form of the invention seen in Fig. 6 again includes elements 10, 26, 11, 30, 16a and 12, as described above; however, the beam reflecting and polarizing structures here comprise mirrors 140 and 141, and transmission polarizers 142 and 143, as shown. The latter are oriented, respectively, at .45° and -45° to the direction of linear polarization of the entering beam 29. Polarizer 142 is located to pass the beams 31a and 48a respectively incident upon and reflected from mirror 140; and polarizer 143 is located to pass the beams 32a and 42a both incident upon and reflected from mirror 141. An example of such a polarizer is that identified as Model HR, a product of Polaroid Corporation. Elements 35, 36 and 37 are also the same as in Fig. 1; and beam 13 is like that previously described.

A preferred "Mach-Zender" version of the invention seen in Fig. 7 also includes elements 10, 26, 11, 30, 16a, 12, 35, 36 and 37 as described above; however, beam reflecting and polarizing structures here each comprise a set of retroreflectors located to separate the beam entering

the set from the beam leaving the set, and a transmission polarizer in the path of that beam. For example, retroreflector set 146 includes 90° angled mirrors 146a and 146b separating beam 31b from beam 48b, and retroreflector set 147 includes 90° angled mirrors 147a and 147b separating beam 32b from beam 42b. A common beam splitter and combiner 30 is employed, as previously, and linear transmission polarizors 150 and 151 can be located either preferably after the retroreflector mirrors (as shown), or between or preceding them. The axis of polarizer 150 is oriented at 0° relative to the plane of Fig. 7 (i.e. the X-direction), and the axis of polarizer 151 is oriented at 90° to the plane of Fig. 7 (i.e., the Z-direction).

A principal advantage of the arrangement of Fig. 7 over that of Fig. 6 is that radiation reflected from the polarizers in Fig. 7 is not recombined in the exit beam, so that the tendency for production of unmodulated or amplitude modulated radiation is reduced.

In both Figs. 6 and 7, the beam 13 is characterized as having orthogonal polarization directions as indicated at 43 and 49 in Fig. 1d.

Beam 155 leaving the splitter-combiner 30 may be returned to a reference detector, or may be employed in a manner like that for which beam 13 is used, i.e. directed througha sample, etc., for subsequent detection, this beam being shown proceeding in a horizontal direction in Fig. 7.

With respect to passage of the beam through the sample, for pure circular dichroism the sample exhibits no difference in absorption for linearly polarized light, no matter how it is oriented in the beam. In the case of linear dichroism, exactly the opposite occurs. The sample, when oriented correctly in the beam, shows a difference in absorption for linearly polarized radiation with one direction of linear polarization from that with the orthogonal direction of linear polarization. If the sample is purely linearly dichroic, it shows no difference in absorption for the circularly

polarized components.

Since the signal for pure linear dichroism is, at a given wavelength, exactly in quadrature with the signal for pure circular dichroism, these two signals can be independently demodulated by the cosine and sine demodulation function respectively.

The alternative forms of the invention seen in Figs. 8 and 9 also include elements 10, 26, 11, 30, 16a, 12, 35, 36 and 37 as referred to above. Beam reflecting structures in Fig. 8 comprise mirrors 160 and 161, and in Fig. 9 comprise retroreflectors 162 and 163 similar to those at 146 and 147 in Fig. 7.

In each of Figs. 8 and 9 beam retarding means is located in the path of at least one of the two beams which are respectively transmitted and reflected by the splitter 30. The retarder illustrated in Fig. 8 comprises a quarter wave plate 166 in the path of the beam transmitted twice by the retarder, i.e. beam paths 32c and 42c. Plate 166 is oriented at plus or minus 45° to the polarization direction of beam 32a. The retarder seen in Fig. 9 comprises a half wave retarder 167 in the path of beam 31d reflected by the splitter 30. Retarder 167 is made as nearly achromatic as possible so that a large spectral range can be covered. Linear polarizer 26 in Fig. 9 may have its axis at either zero or 90° to the plane of the figure, and the axis of retarder 167 is at 45° to that plane. A half wave plate 168 may be located in the path of the beam 32d transmitted by the splitter and operated as a compensator, i.e. to compensate for the path difference caused by the half wave plate and for its dispersion. It is constructed like the plate 167, but is oriented with its axis parallel or perpendicular to the beam polarization so that it does not produce relative phase retardation in the second beam. Matching plate 167 produces phase retardation which substantially matches the phase retardation of either the ordinary or extraordinary ray in the half wave plate 168. If desired, the positions of the retarder 167 and compensator 168 may be interchanged.

The beam splitter in Figs. 6-9 may comprise a thin film of metal on a supporting glass plate, as is conventional. The retarders 166-168 are conventional devices. The purpose of the Figs. 6 - 9 configurations is, of course, to yield a beam 13 with polarization modulation as described in Fig. 4, above.

Referring back to Fig. 1, known elements usable in certain illustrated blocks are identified as follows:

Block 15 --*Mullard TGS Pyroelectric detector (2mm square), a product of Mullard Company, Southampton, England.

Block 19 -- preamplifier Model 225, a product of Princeton Applied Research Labs, Princeton, New Jersey.

Block 20 -- analog to digital computer Model AN 2715M, 15 bit with "sample and hold" option, a product of *Analogic, Wakefield, Massachusetts.

Block 23 -- computer Model 620/L - 105 with 24K memory; 620-06*TTY controller; *TTY (teletypewriter) Model ASR35; 620/L-116 priority interrupt module; and 620-80 buffered I/O controller, products of Varian Data Machines, 2722 Michelson Drive, Irvine, Calif.

Block 23a -- computer to divide $\Delta T(\lambda)$ by $T(\lambda)$; see block 23, used when not collecting data, i.e. time shared for the purpose; or a duplicate machine with smaller memory (4K) and no TTY.

Block 23b -- fringe counter and "central peak" identifier. See block 23a.

Block 24 -- Recorder; see block 23a above.

Block 91 -- Display; *Varian Data Machines Model 620-72 Digital Plotter and Controller.

*Trademark

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In dichroism measurement apparatus the combination that includes:

a) a source of electromagnetic radiation of a relatively broad band of wavelengths λ, and a linear polarizer in the path of said radiation,

b) interferometer means for processing linearly polarized source radiation to provide a beam characterized, for each wavelength, by ellipticity that alternates between left and right circular polarization and between which the beam polarization becomes linear in one direction as the ellipticity alternates from left to right circular polarization, and linear in another direction as the ellipticity alternates from right to left circular polarization, the characteristic frequency ν_a of such alternation varying as a function of the wavelength,

c) a sample space located for effecting passage of the elliptically polarized beam through a dichroic sample in that space, the sample differentially absorbing the alternately polarized radiation of a characteristic set from the wavelengths λ, and

d) a beam intensity detector located in the path of the beam passing from the sample space and characterized as having signal output that varies in intensity with frequency ν_a substantially only when said sample is in said space, said output adapted for processing to produce dichroic spectra varying with wavelength λ,

e) said means comprising a beam splitter located for passing and reflecting source light in two beams, beam reflecting structures in the respective paths of said two beams, said structures being relatively movable, beam retarding means in the path of at least one of said two beams, and

actuating means for effecting such relative movement of said structures to control said frequencies ν_a, said two beams returning toward the splitter as separate but coherent beams and with relative and progressive phase retardation for recombination by the splitter and having orthogonal polarization directions to provide said elliptically polarized beam.

2. The improvement of Claim 1 wherein each of said structures comprises a mirror.

3. The improvement of Claim 1 wherein each of said structures comprises a set of retroreflectors located to separate the beam entering the set from the beam leaving the set.

4. The improvement of Claim 1 wherein said beam retarding means comprises a quarter wave retarder in the path of the beam transmitted twice by the retarder.

5. The improvement of Claim 1 wherein said beam retarding means comprises a half wave retarder in the path of the beam transmitted once by the retarder.

6. The improvement of Claim 5 wherein the beam reflecting structure receiving the beam reflected by the splitter comprises a reflection polarizer.

7. The improvement of Claim 4 including another half wave retarder operated solely as a compensator in the path of the beam transmitted by the beam splitter.

FIG. 1.

FIG. 1a.

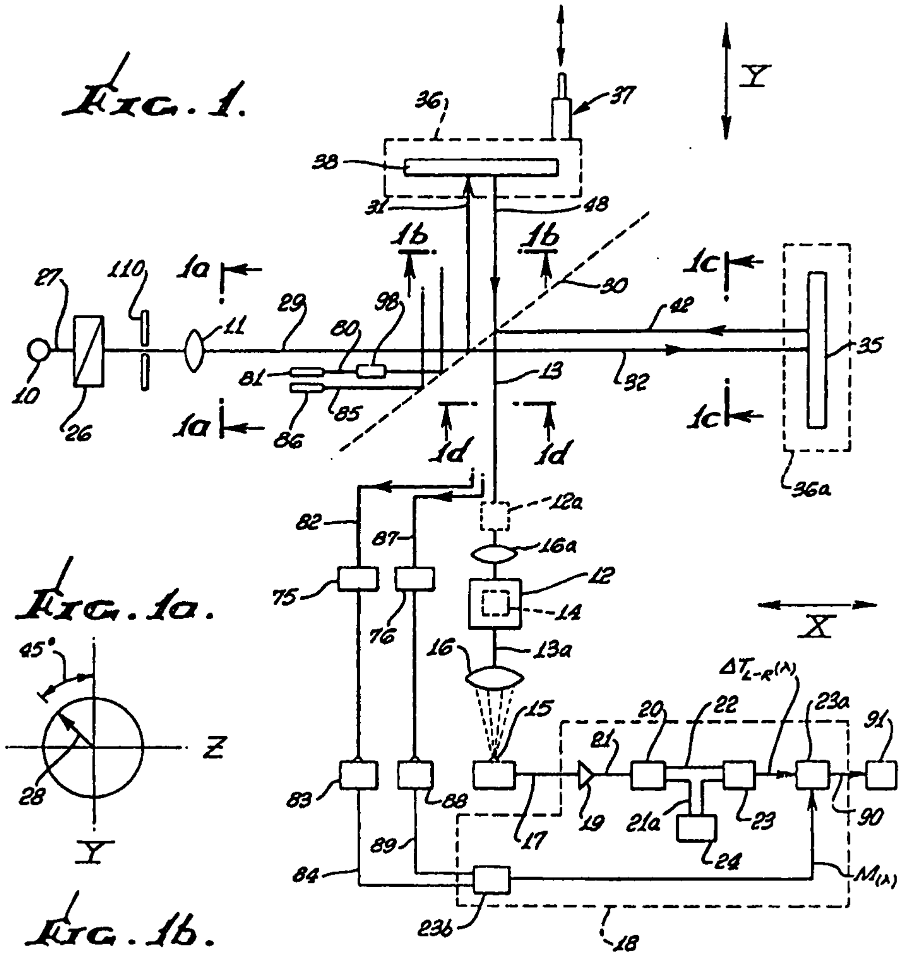

FIG. 1b.

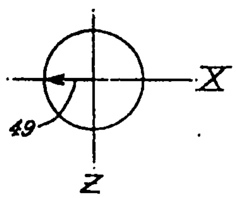

FIG. 1c.

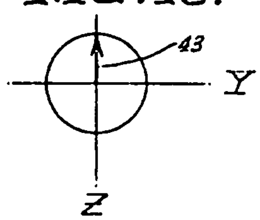

FIG. 1d.

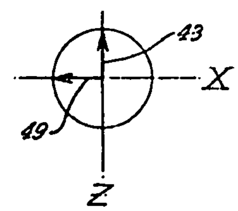

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FIG. 4.

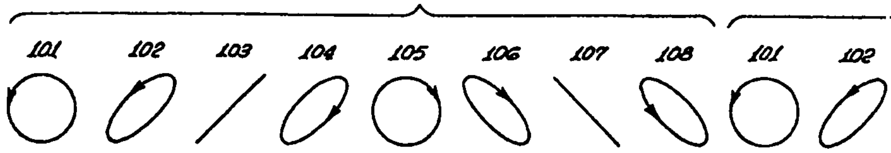

FIG. 5.

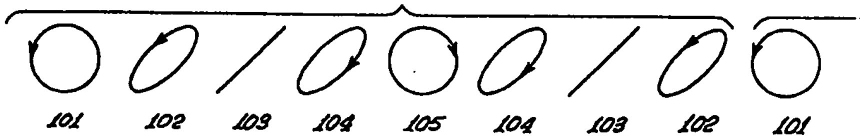

FIG. 2.

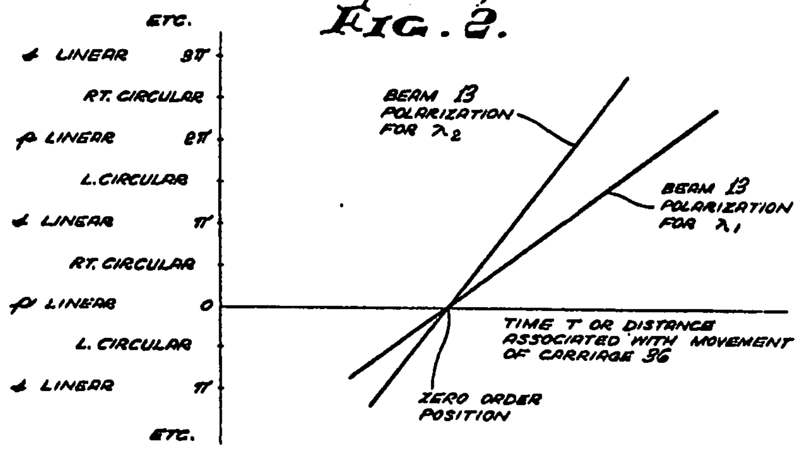

FIG. 3.

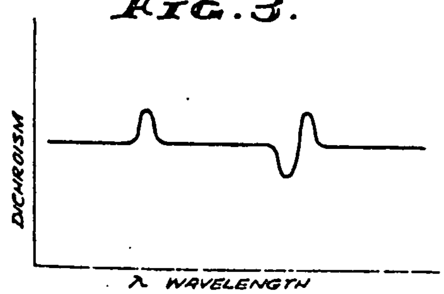

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FIG. 6.

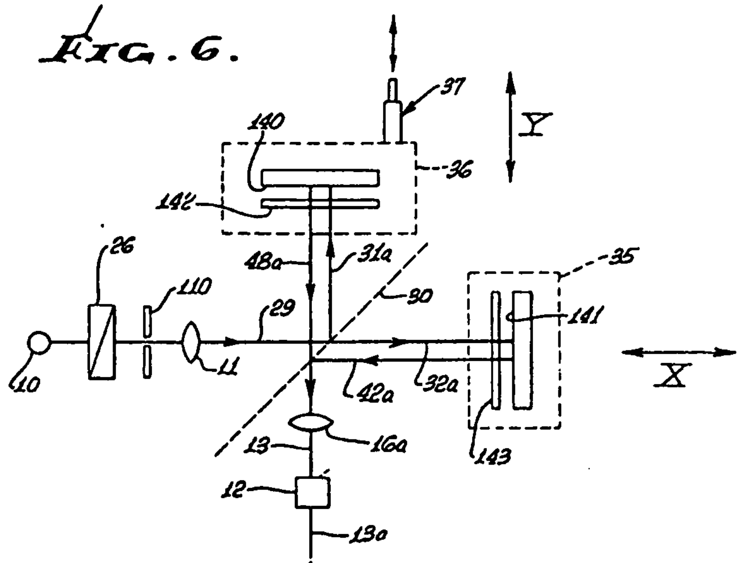

FIG. 7.

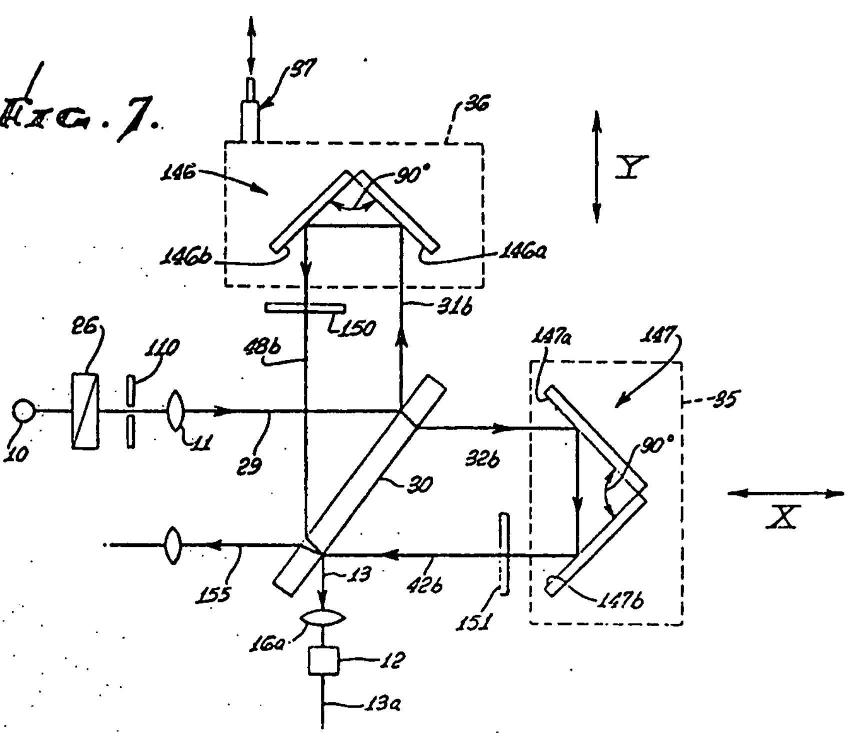

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FIG. 8.

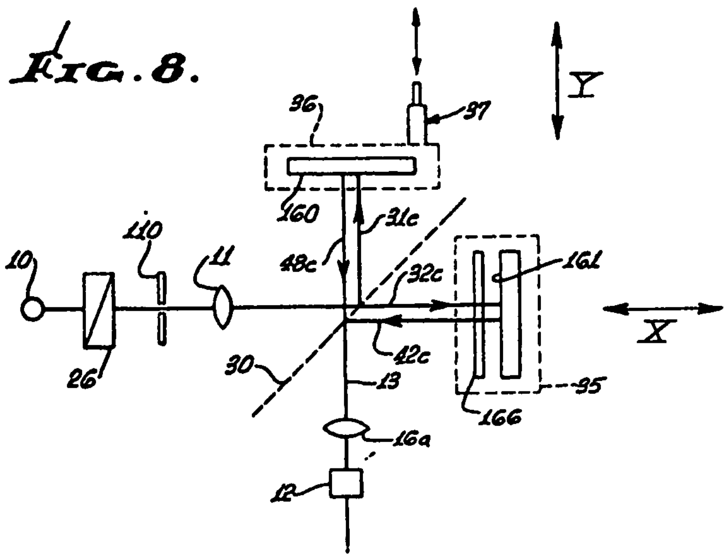
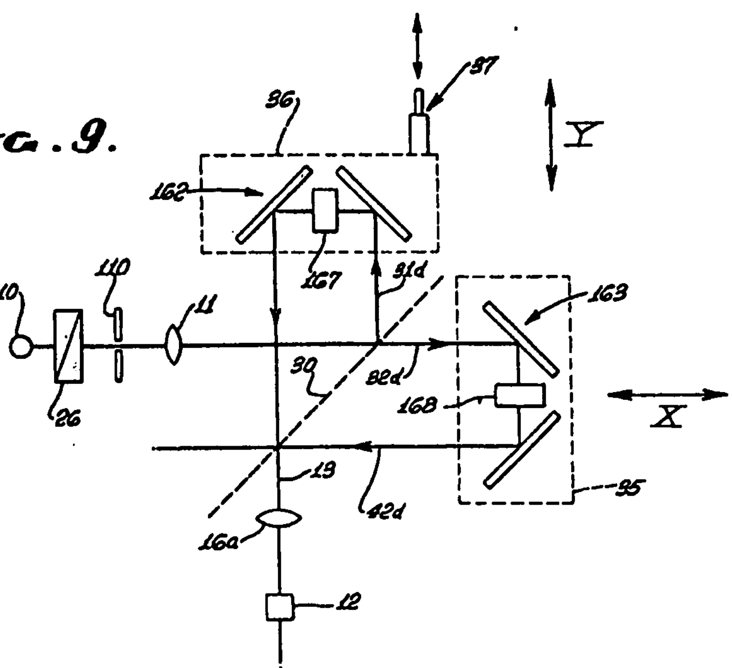


FIG. 9.



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